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Cyanide – The Facts

By Laberge Environmental Services

The Mining Environment Research Group (MERG) is a cooperative working group made up of Federal and Yukon Governments, Yukon First Nations, mining companies, consultants and special interest groups for the promotion of research into mining and environmental issues in the Yukon.

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CYANIDE : THE FACTS

Cyanide is probably one of the most universally recognized poisons. Cyanide contains a carbon atom connected to a nitrogen atom, hence the chemical formula CN. However, the term cyanide is used to refer to a wide array of chemicals containing cyanide. Cyanides can be manufactured but they also occur in nature. In the natural environment, chemicals containing cyanide are produced by a wide range of organisms and approximately 2650 plant species as part of their normal metabolism. Bacteria and fungi are known producers of cyanide. A few species of centipedes, millipedes, insects, beetles, moths and butterflies secrete cyanide for defensive purposes in repelling predators such as toads and birds. Some of the common plants that contain cyanide are cassava, sweet potatoes, corn, lima beans, almonds, radishes, cabbage, kale, brussel sprouts, cauliflower, broccoli, turnips, lettuce, kidney beans, millet, flax, alfalfa, bamboo shoots, and cyanide can be found in the pits or seeds of cherries, plums, apricots, pears and apples. The liver removes the small amounts of cyanide entering our bodies from our daily uptake of the above foods, thus preventing harmful levels of cyanide building up in our systems.

Cyanide is manufactured from ammonia and natural gas, or is a by-product of the manufacture of acrylic fibres and plastics.

What are the forms of Cyanide?

Cyanide can occur in many forms. It can exist as a free ion or can combine with many different elements. Below is a general description of the various categories.

Term	Description	Example
Cyanide ion	the free cyanide ion	CN^-
Molecular HCN	hydrogen cyanide or hydrocyanic acid	HCN
Free Cyanide	includes the cyanide ion and hydrogen cyanide	CN^- + HCN
Simple cyanide	a salt which dissociates to form a cyanide ion	NaCN
Complex cyanide	dissociates to form another cyanide compound	$Au(CN)_2$
WAD cyanide	weak acid dissociable, cyanide that is readily released from cyanide containing compounds when the pH is lowered	$Cd(CN)_2$
SAD cyanide	strong acid dissociable, cyanide that is released from cyanide containing compounds under highly acidic conditions	$Co(CN)_6^{4-}$
Total cyanide	the sum of all of the different forms of cyanide present in a system	

The form of cyanide in water is dependent primarily on pH but is also influenced by temperature, dissolved oxygen, sunlight and the presence of other ions. It has been observed that there are 28 elements which can react with cyanide; producing up to 72 different inorganic complexes.

The form of cyanide usually used in mining is sodium cyanide (NaCN), which is stable in solid form. When mixed with water the pH must be kept above 11 or poisonous hydrogen cyanide (HCN) gas is formed. There are strict safety procedures to be followed when transporting, storing and handling cyanide products.

The toxicity of cyanide depends on the form of cyanide present, ranging from the highly toxic 'free cyanide' to the non or less toxic strong metal complexes.

What is Cyanide used for?

Cyanide compounds have many useful purposes. The word cyanide comes from the Greek word "cyanine" which means blue. Cyanide has been used in synthetic dyes since the 1850s and it is what makes your blue jeans blue.

Due to its toxic nature, cyanide has been used as a fumigant and poison since early time. It has been known for 2000 years that consuming sufficient quantities of bitter almonds, cherry laurel leaves and cassava are poisonous. For example, cherry laurel water was used to poison mammals, birds, reptiles, amphibians, fish and insects. On its more notorious side, cyanide has been used to kill people in judicial executions, genocide, and mass suicide, and has been used as a chemical warfare agent.

Cyanide is also used in the manufacture of nylon, plastic glass, perfume, soaps, fertilizers, paints, animal food supplements, and pharmaceuticals, including heart medication and medical test kits. Cyanide compounds are used in surgical dressings that promote healing and reduce scarring, in anti-cancer preparations, and in drugs to reduce high-blood pressure.

Cyanide is used in electroplating where it 'plates' one type of metal onto another. Examples are silver and gold plated dinnerware and jewellery, and brass plated bathroom fixtures. It also is useful in hardening steel to produce sharp edged tools.

However, its most familiar use in the Yukon is in the mining industry. Over 90% of the gold mined in Canada is extracted using a cyanidation process. Cyanide forms a very stable complex with several metals and has been used since 1887 to extract gold, silver, copper, zinc and molybdenum from ores. Cyanide plays an important role in the mining industry because it allows for the economical recovery of microscopic metals from low grade ore. It is used in the milling process where it dissolves the precious metals through a leaching process or separates minerals during the flotation process. Cyanide has been used in mills at the mines at Faro, Elsa, Mt. Nansen, Mt. Skukum, Ketza, Venus, Arctic Gold and Silver, and at Sä Dena Hes. Heap leaching with cyanide is a newer technology that is currently being utilized at Viceroy Minerals Corporation's Brewery Creek gold mining property near Dawson, and is proposed to be used at the Dublin Gulch property near Mayo.

How does heap leaching work?

In a heap leach operation, a very dilute cyanide leaching solution is sprayed or dripped onto ore stacked on an impermeable pad. As the solution percolates through the heap, precious metals are complexed with the cyanide ion and dissolved. Depending on the height of the pad and size of the ore, it can take up to forty days for the solution to make its way by gravity through the heap. The pregnant solution is recovered, and the precious metals are concentrated with activated carbon. The gold and silver is removed by stripping the carbon utilizing "strip" vessels using a combination of pH, pressure, and temperature, then electroplated onto steel plates. This sludge is removed with high pressure hoses and filtered, dried and smelted into gold/silver bars. The barren solution (the solution that does not contain the precious metals) is recirculated, with cyanide being replenished continuously. The concentration of cyanide necessary to extract gold from the heap is dictated by characteristics of the ore. Viceroy has determined that a cyanide solution containing 35 ppm (parts per million) returning from the heap will allow for good gold recovery. After a certain period of leaching, it is no longer economical to continue leaching residual gold from a heap, and the heap is closed. Residual cyanide remains in the heap either in solution or sorbed (attached) to the ore surface. As a result, the leachate from a spent heap generally contains levels of cyanide above the regulatory limit and will require rinsing and detoxifying prior to abandonment.

What is done with the waste cyanide in tailings ponds and abandoned heap leach pads?

There are several methods to destroy, degrade and detoxify cyanide which involve physical, biological and chemical processes.

Natural Degradation or Attenuation

Natural degradation or attenuation are general terms for all the processes that may reduce cyanide concentrations of a waste without human intervention. These processes that remove cyanide include volatilization, oxidation, bio-degradation, photodecomposition and adsorption (attachment) onto the surfaces of solids. Each mechanism is governed by variables such as pH (a measure of acidity), temperature and water chemistry. The pH of barren water entering tailings or leach ponds is initially high in order to keep cyanide in solution to complex with gold. As the pH naturally decreases below 9, more of the free cyanide is in the form of HCN which has a high vapour pressure and readily evaporates (volatilizes). Oxidation occurs when cyanide reacts with air and water to produce ammonia and bicarbonate, and other species depending on the initial form of cyanide. Biodegradation can occur under either aerobic (with oxygen) or anaerobic (in the absence of oxygen) conditions. There are several species of bacteria that degrade cyanide. Photodecomposition occurs when ultraviolet radiation (sunlight) breaks down cyanide complexes. Iron cyanide compounds are susceptible to this process. Factors such as light penetration (as affected by turbidity, colour and depth), angle of light, intensity and wavelength of light, and cloud cover determine the rate of photodecomposition.

To enhance natural degradation, shallow ponds with large surface areas may be used. This

provides greater contact with atmospheric carbon dioxide which lowers the pH. This in turn increases the rate of conversion to HCN and hence volatilization. Adding air and mixing have similar effects.

Before the mid 1970s, natural degradation was the only treatment method used by the Canadian mining industry for degrading cyanide in tailings ponds. Very little natural degradation appears to take place in the winter under ice cover. Natural degradation and attenuation pathways will remove much of the destruction of free cyanide. However, strongly complexed cyanides are extremely unlikely to release free cyanide at a rate fast enough to be significant, therefore other methods are employed.

Chemical Degradation

Due to the introduction of environmental regulations in the late 1970s, mining operations were required to design and construct additional treatment systems for wastes containing cyanide.

Hydrogen Peroxide Process

This method has become increasingly popular for detoxifying residual cyanide. Hydrogen peroxide reacts with free and WAD cyanides to produce cyanate (CNO^-). Cyanate then decomposes to carbon dioxide and ammonia. The removal of ammonia requires additional treatment. Metal cyanide complexes are precipitated.

Alkaline Chlorination

Alkaline Chlorination has been practiced for many years and involves the addition of chlorine and sodium hydroxide to produce cyanate. This method has recently fallen out of favour due to the difficulty of removing excess chlorine. This method has the potential to form persistent and highly toxic organochlorine compounds from organic compounds in the treated solutions.

Sulphur Dioxide-Air Oxidation

This method is commonly known as the INCO process™ for cyanide destruction. It is the method most commonly used in the Yukon. Cyanide is oxidized at high pH with a combination of sulphur dioxide and air in the presence of copper sulphate to form cyanate, sulphuric acid, and ammonia while releasing metals from cyanide complexes into solution. Again, the removal of ammonia requires further treatment.

Microbial Process

Chemical oxidation of cyanide is expensive regardless of the technique used. An alternative procedure uses cyanide-oxidizing bacteria. Microbial action transforms cyanide to ammonia. Further microbial action will convert ammonia to nitrate. The objective of biological treatment is to increase the rate of these natural transformations.

Research has been done into biological degradation as early as 1913. A wide variety of bacteria and fungi can degrade cyanide compounds and may be useful in the treatment of cyanide wastes. The dried mycelia (tissue) of several species of fungi can degrade cyanide and is sold commercially to detoxify cyanide in industrial wastes. The use of cyanide destroying bacteria is not suitable for all cyanide destruction applications, especially as an on-going treatment method in the mining industry, but has proven successful as treatment of spent leach heaps in Canada, the United States and Australia.

In the Yukon, investigations were conducted at the Brewery Creek Mine near Dawson in 1999 to determine the potential of using cyanide-degrading bacteria as a treatment method in the heaps at the mine-closure stage. Cyanide-degrading bacteria were found to be widespread in the local area and were cultured. The bacteria were placed in columns containing cyanide treated ore, representative of spent ore that would remain on the heap leach pads at closure. To check against other methods, water rinsing and peroxide treatment were applied to two other columns of ore. This research produced encouraging results. Under experimental conditions, microbial destruction was more successful at removing cyanide than the other two treatments. A further benefit to using the biological method was the additional treatment of ammonia by nitrifying bacteria which were also present. Ammonia is also produced in the peroxide and SO_2 treatment but may require the added expense of a further treatment process.

What about spills?

Bulk cyanide is transported in special lined and sealed containers and trucked to the minesite. Spills can occur in a transportation accident or by the accidental release at the minesite. The objective of cleaning up a spill is to immobilize and contain the cyanide and/or convert it to less toxic compounds. The form and amount of cyanide, the area and type of environment affected, the response time and accessibility to the spill will determine how to respond to the problem. Ground spills of solid cyanide, such as sodium cyanide, pose little danger if kept dry and quickly removed. The soil may need to be decontaminated using household bleach or the contaminated layer may need to be removed.

Liquid spills on land, if noticed promptly, may be treated with appropriate oxidizing agents by trained personnel and effectively cleaned up. Some land spills may result in local or widespread contamination of groundwater.

Spills into surface waters are very difficult to treat due to rapid dispersal of the cyanide. The addition of oxidizing agents may further damage the water body. Usually little can be done except to dilute and disperse the spill and encourage natural degradation. Although rapid detoxification of cyanide can occur in the environment, massive kills of freshwater fish by accidental discharges of cyanide wastes have been documented at various sites throughout the world. In Japan in 1981 a large amount of cyanide-containing slag entered a stream from the reservoir of a gold mine as a result of an earthquake. The slag covered the streambed for about 10 kilometres killing all stream biota. Cyanide was detected in the water column for only 3 days after the spill. Within one month flora was establishing on silt covering above-water-stones. After 6 to 7 months, populations of fish, algae and invertebrates had recovered.

To prevent spills and leakage to surface and groundwater, ponds and pads must be lined with impervious material supplemented by secondary containment systems.

What are the detrimental human health effects of cyanide?

Cyanide is a very fast acting poison capable of killing a person within minutes if they are exposed to a lethal dose without prompt first aid treatment. Poisoning occurs through inhalation, skin absorption or swallowing. If cyanide is inhaled, immediate first aid treatment consists of quickly removing the person from the site into fresh air and applying artificial respiration and Amyl Nitrate treatment if the victim is unconscious. Spills on the body should be immediately flushed with copious amounts water while removing contaminated clothing. If ingested and conscious, the victim must be given water to drink and vomiting induced until clear. There have been no documented accidental human deaths due to cyanide poisoning in the Australian and North American mining industries in the 20th century.

People exposed to non-fatal doses normally recover in a short time, and there has been no evidence to suggest that cyanide causes cancer or affects the reproduction system. Unless people are exposed to well over the legal limits for prolonged periods, the evidence suggests that there may be no long term health effects. Cyanide is toxic to humans and mammals because it binds to key iron-containing enzymes required for cells to use oxygen. The tissues are then unable to take up oxygen from the blood and the end result, much like drowning, is suffocation.

As mentioned earlier, cyanide is found naturally in many foods. Cassava, also known as manioc, tapioca, yuca or guacamate, is one of the most important food crops that present cyanide toxicity problems. Cassava is the major food source for people and livestock in many parts of the world and has been under cultivation in tropical America for around 5000 years. The root is usually dried in the sun before consumption, which removes most of the cyanide. However, during periods of drought and famine, cassava is not always prepared properly and poisoning can occur if sufficient quantities are consumed. The symptoms of poisoning include shortness of breath, headache, vertigo, weak rapid pulse, nausea, vomiting and convulsions leading to death.

Cyanide is also contained in cigarette smoke. The US Department of Health has shown that smoke can contain up to 1,600 ppm (parts per million) of cyanide.

The number of fatalities is increasing from smoke inhalation during urban and airplane fires. An increase in toxicity of the fire gases is caused by the use of organic cyanide in plastics in modern construction and furnishings.

What are the environmental impacts of Cyanide?

Cyanide has low persistence in the environment and is not accumulated or stored in any mammals that have been studied. Cyanide biomagnification in food webs has not been reported possibly due to rapid detoxification of sublethal doses, and death at higher doses. Repeated sublethal doses seldom result in cumulative adverse effects and can be tolerated by many

species for long periods. Low levels of cyanide may be harmless under seasonal or other variations that allow organisms to recover and detoxify.

Cyanide persists for long periods in surface waters and soils due to its affinity to complex, sedimentation, microbial metabolism and loss from volatilization, but may persist in groundwater for extended periods of time. More research is required regarding the fate of cyanide in groundwater. The mobility of cyanide in groundwater is dependent on the cyanide metal complex present, the soil type, permeability and soil chemistry. Higher alkalinity appears to increase the mobility of certain cyanide compounds, and alkaline conditions are common in groundwater. Soils containing certain types of clays can increase the attenuation of many cyanide forms, however the cyanide ions themselves do not appear to be strongly adsorbed or retained by soils and can continue moving with the groundwater.

Long term adverse effects associated with mining sites are related primarily to metals rather than cyanide. Cyanide can naturally degrade rapidly in the environment by volatilizing to hydrogen cyanide gas (HCN). This gas is very dangerous when in a closed system such as a warehouse, but the aim is to encourage the gradual release of cyanide to the air in the out-of-doors environment. Cyanide can mix with air and water to produce ammonia and bicarbonate. Ammonia can be toxic in the aquatic system, but (in very small amounts) is an important component of the nitrogen cycle which is vital for plant growth. Consequently low concentrations of ammonia are rapidly assimilated.

Cyanide is toxic to most species in varying amounts. Aquatic organisms are very sensitive to cyanide. Generally, concentrations of free cyanide less than 0.1 mg/L are expected to kill sensitive species in freshwater or the marine environment. Fish have been shown to be the most sensitive aquatic organism, followed by invertebrates. In fact, in some parts of the world, cyanide compounds have been used to collect fish, sometimes illegally as there is no visible evidence of damage to the fish. Fish retrieved from the cyanide poisoned environment can probably be consumed by humans as the residues in the muscle tissues are considered to be low. Algae and macrophytes have been shown to be comparatively tolerant to cyanide.

Birds seem to have varying sensitivity to cyanide. This may be associated with diet rather than size - flesh eating birds appeared more sensitive to cyanide than plant eating birds. Migratory birds have suffered from cyanide poisoning associated with heap leaching facilities and tailings ponds. They may absorb cyanide through their skin when wading or swimming, or ingest it through drinking. The birds may not immediately die if the level is low but can die later when the stomach acids cause the liberation of cyanide if it is a weak acid dissociated (WAD) cyanide compound.

Small mammals, such as rodents, fox, rabbits, bats, etc. have been found dead near cyanide containing tailings ponds, which they have used as a drinking water source. One of the reasons why cyanide is lethal to animals is that there is no known way for cyanide to bioaccumulate in their systems. The prevention of bird and mammal deaths is accomplished by fencing the area, screening or netting the ponds, or decreasing the concentration of cyanide in the ponds. A safe level of cyanide for bird life and mammals is 50 mg/L. Ponds that are too large to be netted can

have floating balls distributed throughout to scare wildlife. Fireworks, lights and music have also been shown to be a deterrent.

The heap leaching operation at Brewery Creek is well fenced and the ponds are covered with nets.

Adverse effects of cyanide on aquatic plants are unlikely at concentrations that cause acute effects to most species of freshwater and marine fish and invertebrates. Low concentrations can sometimes enhance germination and growth. Elevated concentrations can inhibit respiration and lead to the death of aquatic plants.

Cyanide is not a natural constituent of soil and is not strongly retained by the soil when introduced. Microbial reactions may quickly take place to degrade cyanides to carbon dioxide and ammonia under aerobic conditions, or convert cyanide to nitrogen gas compounds that escape to the atmosphere, under anaerobic conditions. Cyanide may also be assimilated by plants or complexed by trace metals present in the soil. The degradation of cyanide through the decomposition of plants that contain natural levels of cyanide appears to be rapid as the levels are very low in the surrounding organic sediments.

Criteria for Cyanide

The toxicity of cyanide is very dependent on its form. Mine effluents, tailings and leach pond water can contain cyanide in many forms ranging from the cyanide ion to strong metal cyanide complexes. Different metal complexes have varying degrees of stability. The toxicity of cyanide compounds depends on the compound's ability to release the cyanide. Some can dissociate easily to form HCN, others breakdown under the effects of sunlight. These and other factors create problems when developing criteria on cyanide discharge limits.

Testing and analyzing of cyanide are also issues because of problems obtaining consistent and reliable results. Analyzing for cyanide can present problems as free cyanide is so reactive and can volatilize readily. This is why any samples to be analyzed for cyanide must be preserved with sodium hydroxide to bring the pH up to 11 or 12. At low concentrations cyanide analysis can be inaccurate due to interferences from other ions and won't necessarily reflect the actual cyanide present. Biologists do not favor the analysis of total cyanide as being meaningless since it poorly correlates with the actual cyanide toxicity. Free cyanide is the most toxic form and when testing for toxicological purposes, analysis for free cyanide should be performed. Testing for weak acid dissociable (WAD) cyanide is also considered a good measure for assessing human and animal toxicity as it measures free cyanide as well as cyanide that is readily released from cyanide-containing complexes when the pH is lowered. When determining the fate of cyanide in the receiving environment, all forms of cyanide and its degradation products should ultimately be analyzed, which obviously, can become very expensive and not practical.

Each mine in the Yukon must abide by a Water Licence issued by the Yukon Territory Water Board. The licence has standards of cyanide concentration that must be met in the effluent before it is discharged to the receiving environment. In general, the discharge limits are 0.5 mg/L

of **total cyanide** and 0.2 mg/L of **WAD cyanide**.

Guidelines for acceptable concentrations of **free cyanide** have been published by the US Department of Fish and Wildlife Service and the Canadian Council of Ministers of the Environment.

	US F&W S	CCME
Sensitive species of aquatic organisms	0.03 mg/L	0.05 mg/L
Birds and livestock	100 mg/kg of diet	
Human Drinking water	0.010 mg/L	0.02 mg/L
Diet	50 mg/kg	
Air	5 mg/m^3	

A Final Word

All of us are in daily contact with cyanide through the foods we eat and the products we use. Although cyanide is extremely toxic, it is definitely beneficial to our lives. With the proper transportation, handling, care and disposal methods, cyanide will not harm ourselves or the environment.

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